Study of UV ageing effects in modern artists' paints with MeV-SIMS

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Abstract

In the present work, alkyd and acrylic self-made paints containing synthetic organic pigments (SOPs) of different chemical classes (phthalocyanine, quinacridone, and diketopyrrolo-pyrrole) were analyzed by Secondary Ion Mass Spectrometry with MeV primary ions (MeV-SIMS) to study the chemical changes that occur due to accelerated UV ageing. MeV-SIMS is an emerging accelerator-based, surface-sensitive mass spectrometry technique that can provide information about the chemical composition in the uppermost layers of materials. Two-component mock-up samples were prepared and aged for two and four months, to mimic environmental ageing over periods of one and two years. The obtained results show that the studied SOPs are stable under the accelerated ageing conditions used in this study and that they can be easily identified in aged paints, while the binder components undergo structural changes due to the photodegradation processes. The kinetics of binder degradation were found to be dependent on the pigment present in the paint, with phthalocyanines having the highest photostabilizing effect among the pigments studied. In addition, the acrylic binder exhibited slightly higher stability to UV ageing than the alkyd medium. This study allowed the identification of SOPs and binders in the selected contemporary artworks, which date from different periods and belong to both outdoor and indoor collections.

Keywords: MeV-SIMS, synthetic organic pigments, alkyd, acryl, UV ageing, artwork

1. Introduction

Synthetic materials were introduced to the paint market in the early 20th century, have continuously grown in diversity ever since, and have thus spread to various application areas. The development of synthetic organic pigments (SOPs) for paint colorants and synthetic resins used as binding media has enabled significant advancement in paint products. Excellent chromatic properties and high chemical stability were achieved as well as faster drying times and improved esthetic properties compared to traditional materials [1]. The high compatibility of SOPs with synthetic resins, such as alkyds and acrylics, makes them dominant in the colorant market [2]. As a result, their frequent use by contemporary artists led to numerous scientific studies on the characterization of these materials and investigation of their long-term stability and durability for conservation purposes [3]–[5]. The latter focused on the studies of photostability [6]–[8], thermal and chemical stability after exposure to atmospheric pollutants [9], [10] as well as the influence of SOPs on the stability of binding media [10]–[12].

In the case of outdoor artworks, one of the primary causes of paint degradation, and consequent changes in the physical and mechanical properties is exposure to solar radiation. Dissociation of chemical bonds in organic compounds due to exposure to ultraviolet radiation, in combination with the presence of oxygen, promotes photo-oxidative reactions in the material [13]. The most frequently used methods for the studies in degradation mechanisms and chemical changes of paint materials today are Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), FTIR with attenuated total reflection mode (FTIR-ATR), UV-Vis spectroscopy and Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) [2]–[4], [6], [12], [13]. Raman and infrared spectroscopies are complementary techniques, which can be used in situ with portable instruments and can be suitable for investigating certain chemical processes that occur in the surface layer of the material. Nevertheless, they often fail when the exact identification of SOPs in real

artworks is required [2], [14]. In many cases, only the identification of the chemical class of a particular SOP in the paint is possible. For Py-GC/MS, on the other hand, small amounts of the material have to be taken from the art object and consumed during the analysis. However, this technique is particularly suitable for studies of the degradation products due to ageing and for studies of the material thermal stability [12]. The identification of the binder and SOPs in the paint sample by Py-GC/MS often requires different pyrolysis temperatures, meaning that more than one sample is needed for the analysis.

Secondary ion mass spectrometry with MeV primary ions (MeV-SIMS), has emerged as a novel method for the assessment of the chemical composition of artists' paints and a powerful technique in cultural heritage studies. It has been successfully used for the identification of SOPs in paint materials and for molecular imaging of modern inks and paints [15]–[17]. Irradiating the sample surface with an ion beam in the MeV energy range causes desorption of intact molecules from the sample surface through electronic sputtering, leading to significantly higher secondary molecular ion yields compared to keV-SIMS [18]. This type of interaction consequently results in less fragmentation of desorbed surface species and enables a straightforward interpretation of the mass spectra for the molecular characterization of the sample surface, making it especially suitable for the exact identification of SOPs.

In the present work artificially aged alkyd and acrylic self-made paints, containing the SOPs of different chemical classes (phthalocyanine, quinacridone and diketopyrrolo-pyrrole), were studied with MeV-SIMS which is a highly surface-sensitive technique (with a few monolayers probing depth), in order to assess chemical changes that are taking place in the uppermost layers of the paint. For this purpose, the paint samples were exposed to conditions that are typical for outdoor solar radiation (accelerated UV ageing in the range between 295 and ca. 3000 nm, full nominal irradiance 910 W/m^2) for two and four months. The aim of this study was to evaluate the photostability of the paints under accelerated solar radiation, particularly SOPs and binders, as well as to assess whether the exact identification of SOPs can still be performed on aged paints. Additionally, the aim was to further facilitate paint analysis with MeV-SIMS for the identification of SOPs and binders commonly found in contemporary artworks that have been exposed to environmental conditions and are expected to have undergone certain chemical changes. This knowledge is of particular importance in cultural heritage studies and for conservation and preservation purposes. Furthermore, the addition of MeV-SIMS to the common ion beam techniques (PIXE, RBS, PIGE) provided by accelerators and already used for the analysis of inorganic pigments in the cultural heritage objects, opens the possibility to analyze organic components of the paints, especially SOPs. This makes accelerator-based techniques applicable not only for modern and contemporary paints analysis but also for modern inks and some traditional materials, e.g., analysis of binders such as tempera and oil.

2. Experimental

2.1 Materials

For a systematic study of the photodegradation phenomena that are taking place in the uppermost layers of paints, two-component mock-up samples were prepared, containing the selected SOPs mixed with an alkyd or acrylic binder. These types of samples were chosen over commercial products to avoid any interactions that may arise due to the presence of other constituents (additives) that vary significantly in composition and concentration from one manufacturer to another.

The selected pigment powders were: i) three different polymorphs of copper phthalocyanine blue pigments (CuPh), PB15:1, PB15:3 and PB15:6 (α, β, and ε, respectively), ii) metal-free phthalocyanine (Ph) PB16, iii) chlorinated CuPh green pigment PG7, iv) violet (PV19) and red (PR122) quinacridone pigments, and v) two red diketopyrrolo pyrrole pigments (DPP), PR254 and PR255. All pigment powders were provided from Kremer Pigmente (Germany). The pigments were manually mixed with two types of binding media: i) alkyd resin Medium 4 (Lukas, Germany), with a structure derived from pentaerythritol, phthalic anhydride, and fatty acids (azelaic (2C9:0), palmitic (C16:0), oleic (C18:1), linoleic (C18:2), and stearic (C18:0)) as main constituents [13], and ii) Plextol D498 (Kremer Pigmente, Germany) which is a p(nBA/MMA) copolymer, a co-emulsion of poly(butyl acrylate-methyl methacrylate) [8].

The pigment to binder ratio in the prepared paints varied depending on the consistency of the produced paint. For the alkyd paints, this ratio was between 1:6 and 1:10 as presented in Table 1. The acrylic mock-up paints were prepared in a wider range of pigment to binder ratios (Table 1), from 1:3 for blue and green pigments to 1:70 for PV19 pigment. The paints were then cast in a 150 μm thick layer on microscope glass slides, which served as an inert support during ageing, and were left for 15 days to dry under ambient conditions. After drying, the samples were exposed to accelerated solar radiation for two (UV1) and four months (UV2).

Table 1. List of materials used for the preparation of the alkyd and acrylic mock-up paints containing the selected SOPs with given ratios of the two paint components.

Pigment class	Chemical formula	Pigment C.I. generic name	Molecular weight (g/mol)	Pigment-alkyd binder ratio	Pigment-acrylic binder ratio
Phthalocyanine	$C_{32}H_{16}CuN_8$, $(0.5 - 1\ Cl)$	PB15:1	611.52	1:6	1:3
	$C_{32}H_{16}CuN_8$	PB15:3	576.11	1:6	1:3
	$C_{32}H_{16}CuN_8$	PB15:6	576.11	1:6	1:3
	$C_{32}H_{18}N_8$ metal-free	PB16	514.58	1:6	1:3
	$C_{32}Cl_{16}CuN_8$ Cl substituted on benzene rings	PG7	1127.15	1:6	1:3
Quinacridone	$C_{20}H_{12}N_2O_2$ $R_1 = H$ $R_2 = H$	PV19	312.34	1:10	1:70
	$C_{22}H_{16}N_2O_2$ $R_1 = CH_3$ $R_2 = CH_3$	PR122	340.40	1:10	N/A
Diketopyrrolo-pyrrole	$C_{18}H_{10}Cl_2N_2O_2$ $R_1 = Cl$ $R_2 = Cl$	PR254	357.20	1:10	1:10
	$C_{18}H_{12}N_2O_2$ $R_1 = H$ $R_2 = H$	PR255	288.32	1:10	1:10
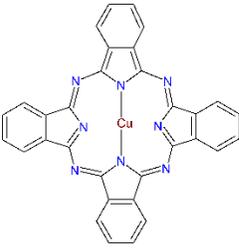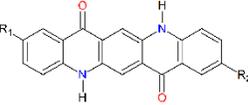
Binder	Chemical composition	Product name
Alkyd resin	oil-modified polyester	Alkyd Medium 4
Acrylic emulsion	p(nBA/MMA) copolymer	Plextol D498

Subsequently, three contemporary artworks that are expected to have undergone ageing processes were analyzed with MeV-SIMS and the results obtained on model samples were applied in the identification of SOPs and binders. The first studied object was the "MNB" painting by the Croatian artist Julije Knifer, from the collection of the Museum of Contemporary Art in Zagreb, Croatia. It is an acrylic painting on canvas, painted in 1970 with the motif of a meander in blue and black color, presented in Figure 1a. Although the painting is kept in the Museum and is not exposed to direct sunlight, it was considered for a test case due to its history and high likelihood that it has been exposed to various environmental conditions over time (e.g., low-quality lighting conditions which may include the UV component, relocation of the Museum and its holdings in 2009, daylight expositions, transport to different exhibition venues, etc.). Two areas of the painting were sampled for analysis, the blue and black paints. The second artwork analyzed was an iron outdoor sculpture "Plavi cvijet" that was created in 2000 by Vjenceslav Richter and belongs to the "Richter Collection" from the Museum of Contemporary Art in Zagreb, Croatia (Figure 1b). The dark blue paint on the circular components was sampled from the sculpture for analysis. The third artwork is an outdoor mural painting "La dolcezza dell'abisso" (declared as an acrylic) created in 1991 by Santo Tomaino, from the open-air Museo d'Arte Contemporanea all'Aperto di Maglione (M.A.C.A.M.) in Maglione, Italy. The dark blue sample from the bottom left region was taken for the analysis (marked in red, Figure 1c).
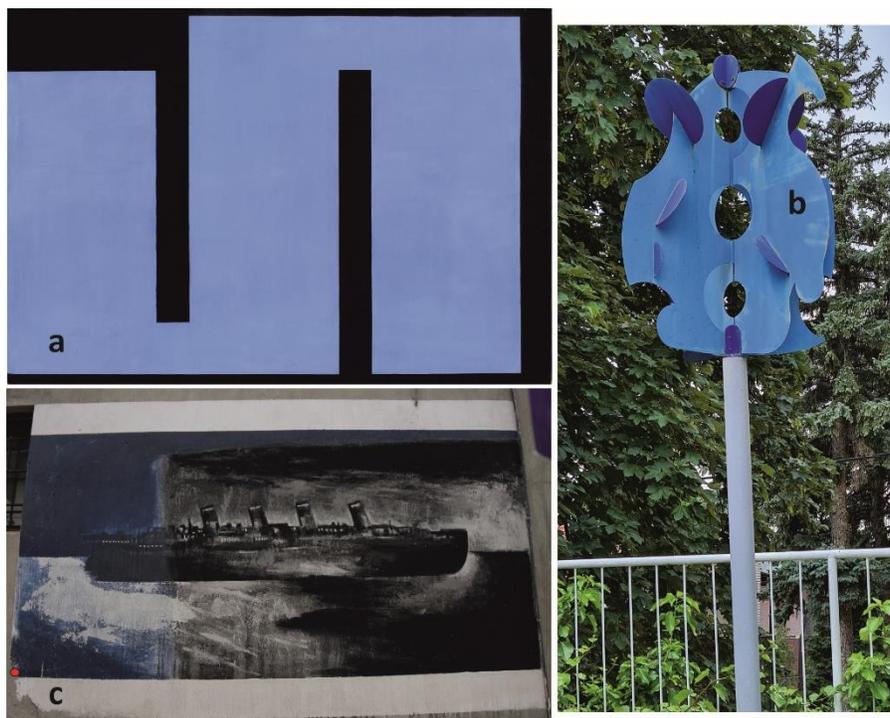
Fig. 1. The "MNB" painting (1970) by Julije Knifer (a), the outdoor sculpture "Plavi cvijet" (2000) by Vjenceslav Richter (b), and the outdoor mural painting "La dolcezza dell'abisso" (1991) by Santo Tomaino (c). Photos by Boris Cvjetanović (Courtesy of the Museum of Contemporary Art, Zagreb, Croatia) (a), Matea Krmpotić (b) and Marta Anghelone (c).

2.2 Artificial ageing

As already described in the work of Anghelone et al. [19], two intervals of exposure in the solar simulator at 910 W/m^2 were selected: two months (UV1), and four months (UV2). These intervals roughly correspond to one and two years of exposure under natural outdoor sunlight, considering the radiant exposure defined as the time integral of irradiance (W x s/m^2 = J/m^2) of yearly natural outdoor conditions. The day/night cycles occurring in natural ageing were not considered in this study. The exposure to artificial solar radiation was continuous over time, therefore, the ageing conditions applied here must be considered as "accelerated" artificial ageing.

A Xenon Arc Simulator SOL2/500 (Dr. Hönle UV Technology, Germany) equipped with an H2 filter, emission spectrum between 295 and ca. 3000 nm and full nominal irradiance of 910 W/m^2 was used. Temperature and relative humidity (RH) were not customizable in the chamber. Temperature values of T = 40 °C and RH of 10% were measured by means of AQL S500 (Aeroqual Limited, New Zealand) sensors. The irradiance of the Xenon lamp in the Vis and UV-A range was measured with a UV-Meter Basic (Dr. Hönle, Germany).

2.3 Measurements and data treatment

Small flakes of the aged two-component paints were taken with a clean stainless-steel scalpel from the glass slides and pressed with a flat and clean aluminum plate into an indium substrate for measurement (99.99% in tear drops, Alpha Aesar, USA). The same procedure was performed for the measurement of the blue and black paint samples from the "MNB" painting and the blue paint sample from the "La dolcezza dell'abisso" mural painting. The blue paint sample from the "Plavi cvijet" sculpture was fixed between two indium plates and cut to produce a cross-section.

Samples were measured using MeV time-of-flight secondary ion mass spectrometry (MeV-TOF-SIMS) at the heavy ion microprobe at the Ruđer Bošković Institute. The measurements were performed in a pulsed-beam positive-ion mode with 5 MeV Si^{4+} primary ions for the analysis of unaged and aged two-component mock-ups as well as for the "MNB" painting and "La dolcezza dell'abisso" mural painting. START signal for measuring the time-of-flight of sputtered ions was defined by the pulsed beam, while the STOP signal was defined by secondary ions reaching the microchannel plate (MCP) detector at the end of the TOF tube. An extraction voltage of +5 kV was applied to the sample holder. Measurements were performed in vacuum ($10^{-6} - 10^{-7}$ mbar). Data was collected from a region of approximately 100 × 100 μm^2, with a beam spot focused to 10 × 10 μm^2 on the target. Measurement of the cross-section sample of "Plavi cvijet" was performed using an 8 MeV Si^{4+} primary ion beam for a higher ionization yield and better spatial resolution. The beam spot on the target was focused to 5 x 5 μm^2 and scanned over an area of 175 x 145 μm^2. More details about the measurement, together with the 2D maps of the cross-sections can be found in reference [16]. The sample surface was oriented 45° towards the incident beam and secondary molecular ions were extracted from the sample by an extractor tip that was positioned perpendicular to the sample surface at a distance of 10 mm. Due to the sample surface roughness, the extraction angle was optimized for each performed measurement to achieve a maximum secondary molecular ion yield. A Multi-Stop Time-to-Digital Converter (TDC) Data Acquisition System in a deflection start mode was used with a 100 μs delay between two heavy ion pulses (duration of 4 ns). All experimental and data acquisition parameters were controlled with the in-house SPECTOR software package [20]–[22]. The spectra were calibrated using MATLAB software (Version 2011) as described in Krmpotić et al. [17]. The mass resolution, M/ΔM, of the obtained spectra was up to 500, as published in Tadić et al. [20]. The mMass-Open Source Mass Spectrometry Tool was used for spectra analysis (version 5.5.0) [23]. For spectra comparison, the base peak normalization method was employed.

The blue and black samples of the "MNB" painting were additionally measured by Particle Induced X-ray Emission (PIXE) for the determination of elemental composition and possible identification of inorganic pigments. The measurement was also performed on the heavy-ion microprobe at Ruđer Bošković Institute with a 2 MeV proton beam. Emitted X-rays were detected using a large surface area Si(Li) detector positioned at a 45° angle to the beam normal. The scanned surface area was approximately 100×100 μm^2, with the beam spot on the target focused to 2×2 μm^2.

3. Results and Discussion

3.1 Aged two-component mock-up paints

Mass spectra were collected for all prepared two-component mock-up paints before artificial ageing in order to characterize the detected species in their original chemical form. The pigment-characteristic peaks (molecular ions and larger characteristic fragment ions) were observed in both alkyd and acrylic media containing phthalocyanine (PB15:1, PB15:3, PB15:6, PB16, and PG7), quinacridone (PV19 and PR122), and diketopyrrolo-pyrrole (PR254 and PR255) pigments. The mass spectra of alkyd and acrylic paints, with phthalocyanine PB15:3 pigment as an example, are presented in Figure 2. As reported in our earlier work [17], the molecular ion peaks of the chlorinated phthalocyanine PG7 pigment ($m/z > 1000$) were not detected in the unaged samples due to the fact that the sensitivity of the ToF-SIMS technique decreases with increasing mass of the secondary ions [24]. Lower sensitivity for higher mass ions is more of an issue for the detection of SOPs in matrices where pigment concentrations are low. In this regard, only larger pigment-characteristic fragments were detected for paints with the PG7 pigment. The binder-characteristic peaks were detected only in the alkyd paints, in the mass region above m/z 100, with a strong peak at m/z 105 (Figure 2a), which corresponds to the phthalic anhydride fragment, $C_7H_5O^+$ [17]. The phthalic anhydride component of the alkyd resin, $C_8H_5O_3^+$, was also detected at m/z 149 (Figure 2a) [17]. Acryl-characteristic peaks in the unaged acrylic paints were only observed in the lower mass region, below m/z 100 (presented in Figure 2b).
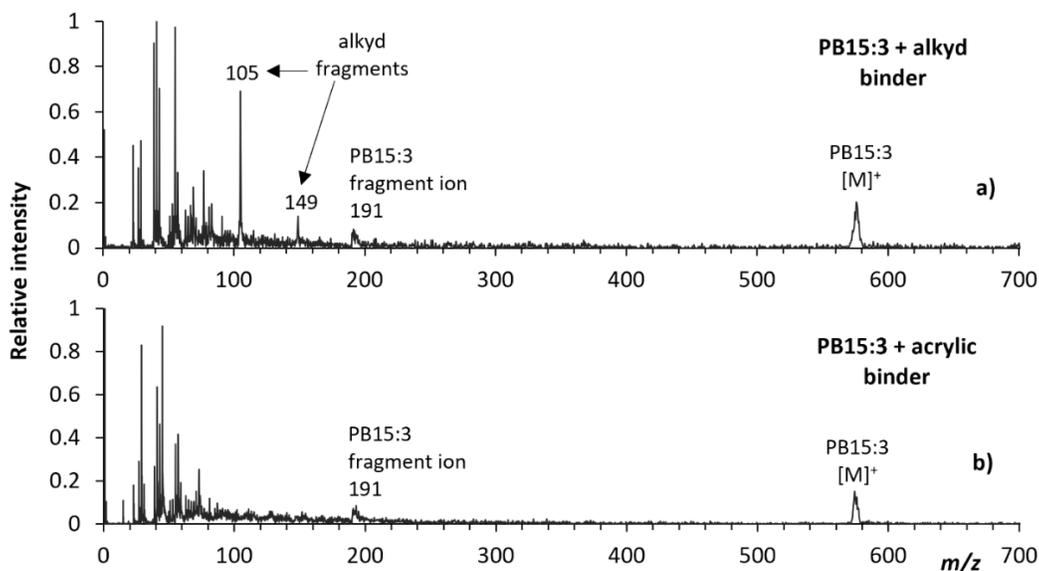
Fig. 2. MeV-SIMS spectra (5 MeV Si[4+], positive-ion mode) of the unaged self-made paints containing PB15:3 pigment in alkyd binder (a), and acrylic binder (b).

In the artificially aged alkyd and acrylic two-component paints, the molecular ions and characteristic fragments of all investigated pigments were detected, which was confirmed by spectra comparison with unaged samples of mock-up paints and pure pigment powders. An increase in the relative intensities of these species with exposure time was observed, indicating that no significant structural changes occurred in the pigment components of the paints in both two (UV1) and four months aged (UV2) samples. This

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confirms the chemical stability of the studied phthalocyanine, quinacridone, and DPP pigments under accelerated UV irradiation ageing conditions, which is in agreement with previous studies [4], [6], [19]. As can be seen in Figures 3-5, the increase in the relative intensities of the pigment-characteristic peaks (especially the molecular ion species) in the UV-aged compared to the unaged paints indicates that the degradation process of the binder is taking place. This is also in agreement with the results reported in the literature [4], [19], [25], [26]. Enrichment of the pigment relative to the binder at the paint surface is a result of the formation of volatile, low molecular weight species that are lost due to photocleavage reactions in the binder, thus reducing the binder content at the paint surface [5], [19]. As a result, the identification of the SOPs with MeV-SIMS in the aged paints is facilitated and more straightforward. It is worth emphasizing that the pigment enrichment on the surface due to ageing is particularly beneficent for the detection of higher molecular-mass pigments with MeV-SIMS, such as already mentioned chlorine substituted CuPh, PG7, due to decreased sensitivity for higher mass species. With the relative increase in the pigment concentration on the surface, we were able to detect the PG7 molecular ions (at m/z 1127, 1056, 986) [17] in the aged alkyd paints with increasing relative intensity as the ageing time increased from two- (UV1) to four-month period (UV2). In the acrylic paint, the molecular ions of PG7 were detected only in the four-month aged paint which can be seen as an indication of higher stability of the acrylic binder compared to the alkyd [25]. The fact that the initial pigment concentration was higher in the acrylic mock-up (1:3 ratio) than in the alkyd paint (1:6) supports this observation.

Relative intensities of the alkyd-characteristic peaks (m/z 105 and 149) were found to decrease significantly in the UV1 samples (Figures 3c-5c) and to disappear in the UV2 paints (Figures 3d and 5d). New species were detected in all alkyd paints at m/z 155, 173, 327 and 482, regardless of the pigment included in the mixture (as listed in Table 2 for the UV2 aged samples), with the peak at m/z 155 having the highest relative intensity among them. Since the occurrence of these species was found to be independent of the pigment present in the paint, they can be attributed to the degradation products of the alkyd binder. This further confirms the initial observation that the alkyd component of the paint undergoes photo-radical reactions, such as chain scission, cross-linking, and oxidation. Whether these degradation products are formed in the two- (UV1) or four-month aged paint (UV2) depends on the pigment present in the mixture. In the phthalocyanine-containing paints (PB15:1. PB15:3, PB15:6, PB16, and PG7) these degradation products were detected in the UV2 samples (presented for PB16 paint in Figure 2d), while in the quinacridone (PV19 and PR122) and DPP-containing paints (PR254 and PR255) they were already detected in the UV1 samples (Figures 4c and 5c for PV19 and PR255 alkyd paints, respectively). The observed longer exposure time needed for the formation of the alkyd degradation products in phthalocyanine-containing paints confirms their higher photostabilizing effect in comparison to quinacridone and DPP pigments [19].
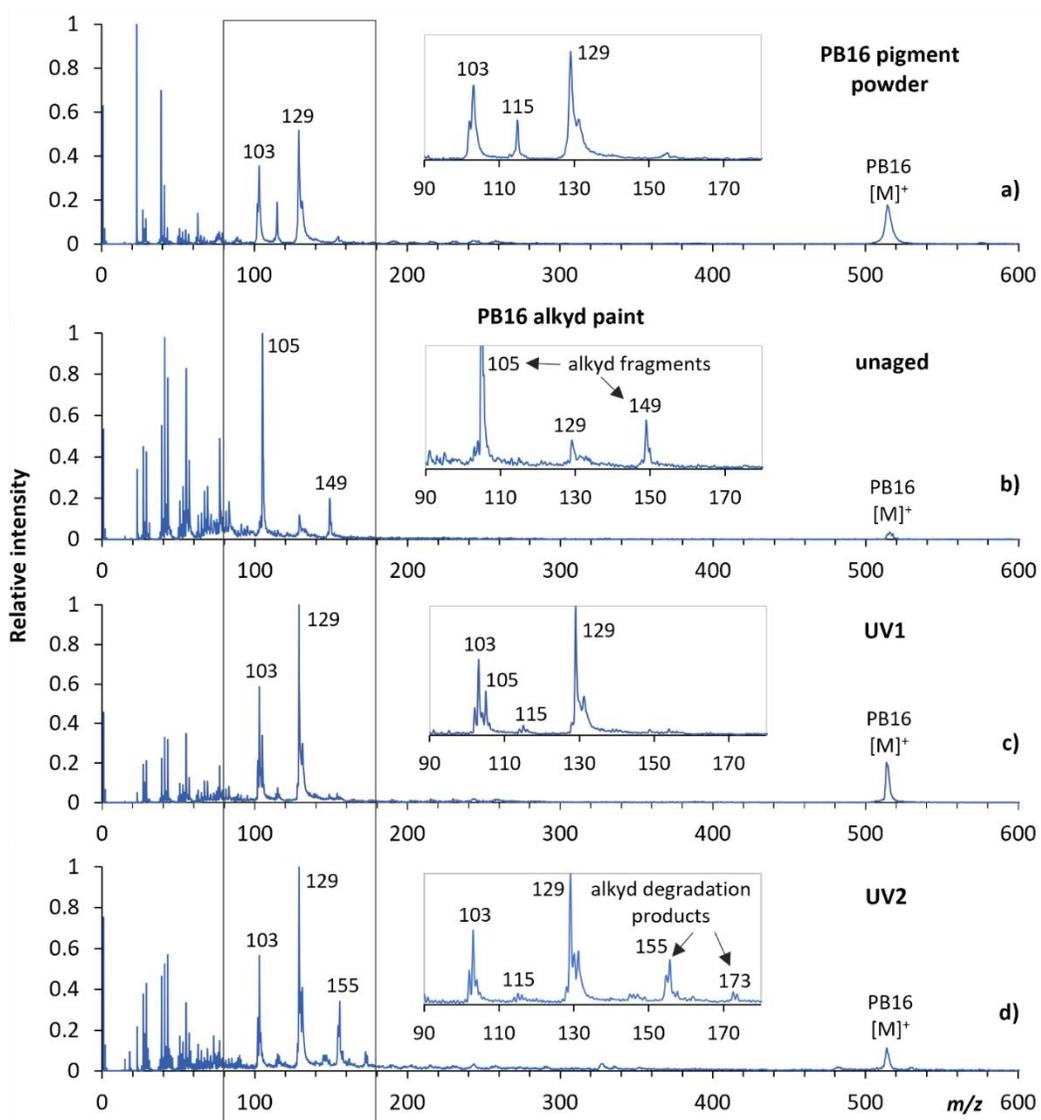
Fig. 3. MeV-SIMS spectra (5 MeV Si^{4+}, positive-ion mode) of the phthalocyanine PB16 pigment powder as a reference (a), and self-made alkyd paint with PB16: unaged (b), two-month aged paint, UV1 (c), and four-month aged paint, UV2 (d). For each spectrum, the *m/z* region between 90 and 180, where the pigment- and binder-characteristic fragments are the most abundant, is also presented as in insert.
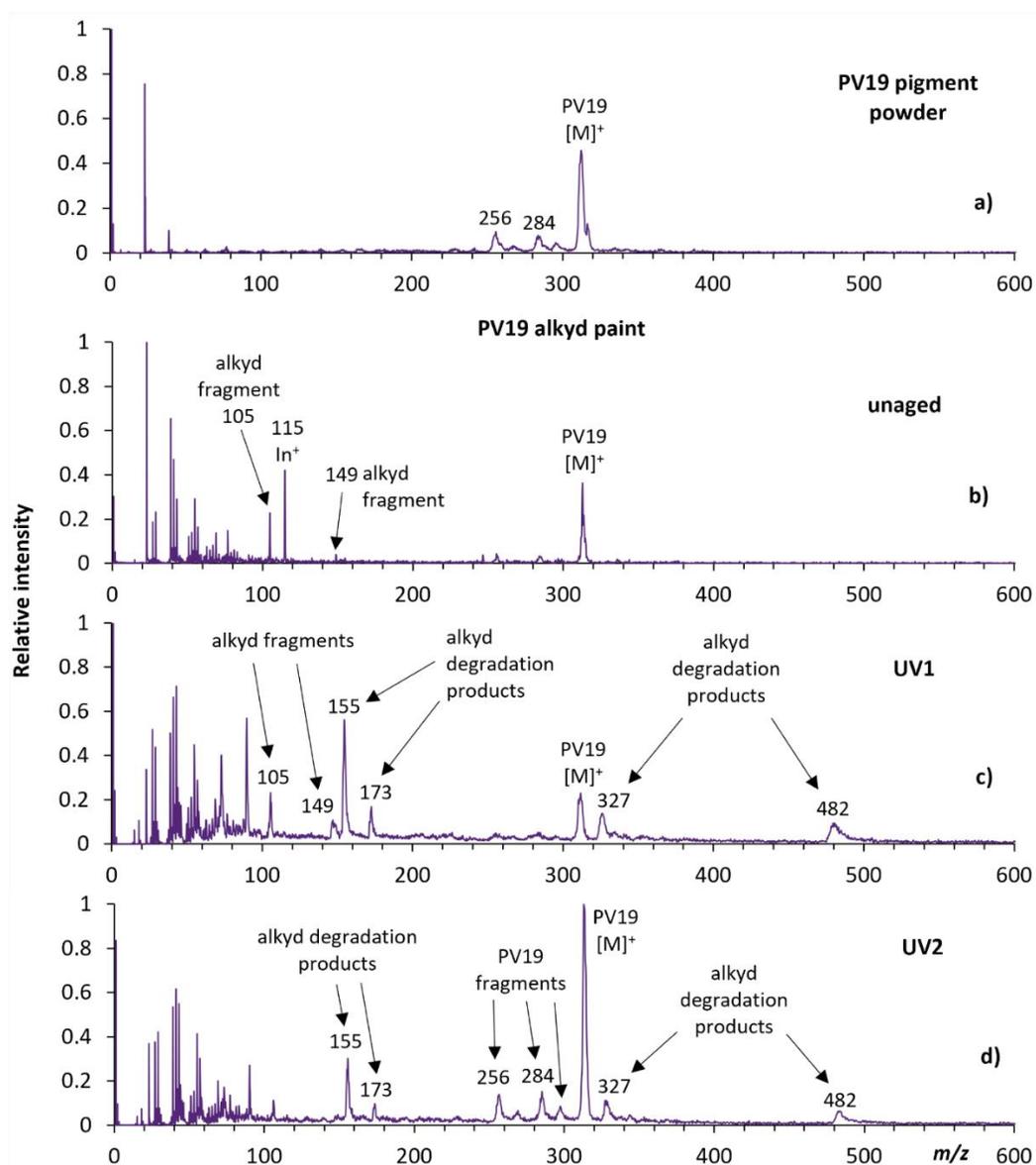
Fig. 4. MeV-SIMS spectra (5 MeV Si^{4+}, positive-ion mode) of the quinacridone PV19 pigment powder as a reference (a), and self-made alkyd paint with PV19: unaged (b), two-month aged paint, UV1 (c), and four-month aged paint, UV2 (d).
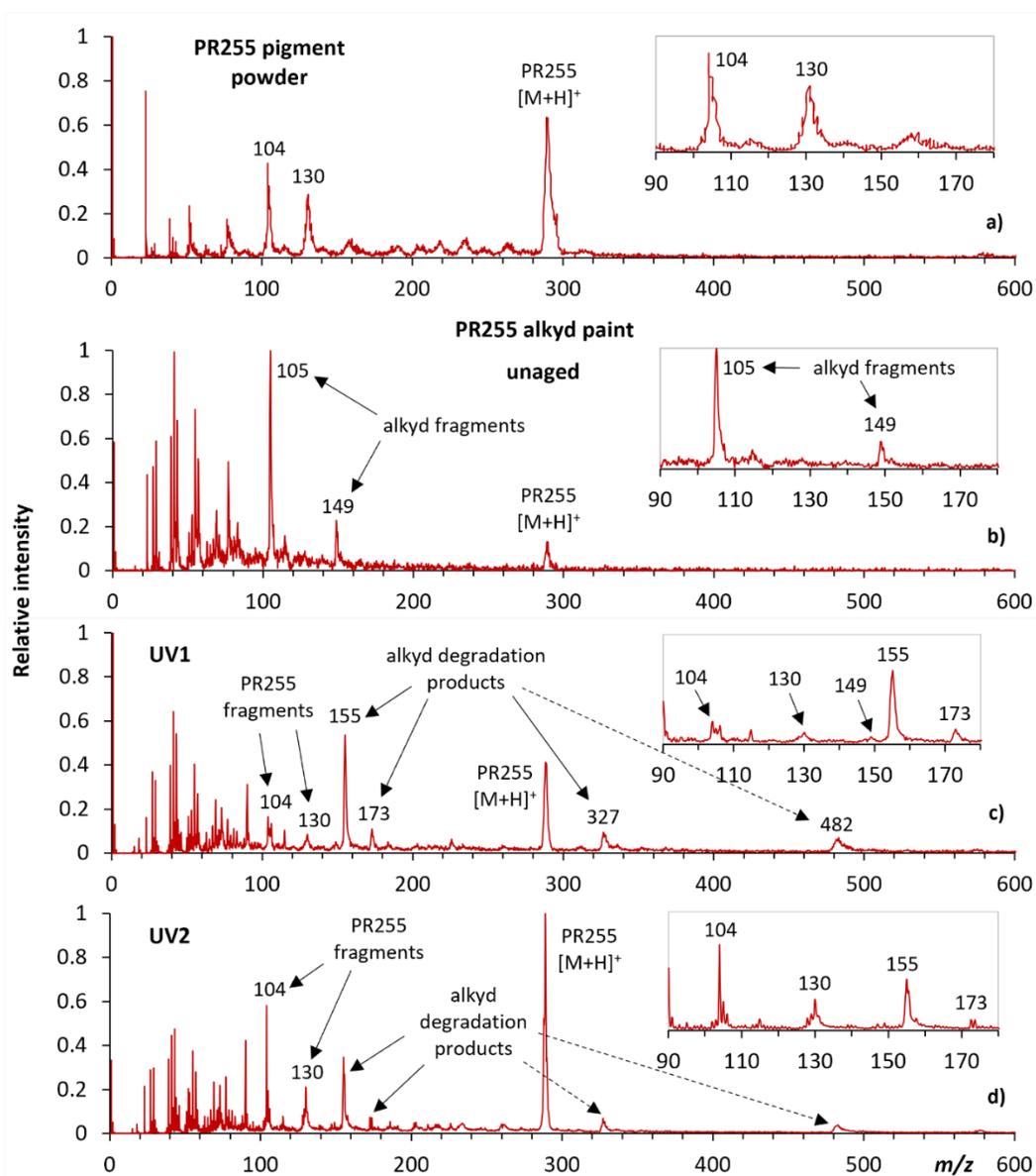
Fig. 5. MeV-SIMS spectra (5 MeV Si^{4+}, positive-ion mode) of the DPP PR255 pigment powder as a reference (a), and self-made alkyd paint with PR255: unaged (b), two-month aged paint, UV1 (c), and four-month aged paint, UV2 (d). For each spectrum, the *m/z* region between 90 and 180, where the pigment- and binder-characteristic fragments are the most abundant, is also presented as an insert.

In the aged acrylic paints, the occurrence of peaks in the mass spectra associated with the non-pigment component showed greater variation between samples that was not observed in the aged alkyd paints, indicating that the studied pigments influence the kinetics of the acrylate degradation to various degrees. This effect was also observed for the acrylic binder containing different SOPs in the study by Ciccola and co-workers [4], where e.g., the lactone formation, which is a favorable process both at the surface and in the bulk, was pronounced for anthraquinone and DPP pigments but was very faint for phthalocyanines. As presented in Table 2 for the UV2 acrylic paints, the degradation products at *m/z* 155 were detected in the paints containing PB16, PV19, PR254, and PR255 pigments, at *m/z* 150 only for the PV19 containing paint, and at *m/z* 288 only for the PB15:1 containing paint. The peak at *m/z* 155 that was detected in almost all aged acrylates could correspond to a unit of the p(nBA/MMA) copolymer formed in the ester side-chain loss (OC$_4$H$_9$ loss from the nBA-MMA dimer) which is known to be a principal mechanism of

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photodegradation for acrylic polymers taking place directly in the surface layer [27]. The presence of peaks at m/z 150 and 288 in the aged PV19 and PB15:1 acrylic paint, respectively, suggests that degradation products may be formed due to pigment-binder interaction. Species at m/z 313, 341, 369, and a group of peaks with m/z values ranging between 523 and 607, were detected in the UV1 and UV2 aged paints of the DPP pigments (PR254 and PR255; Figure 6b). These higher-mass species, that indicate polymer chain scission and formation of products through cross-linking and oxidation processes, confirm that DPP pigments are promoting the degradation process of the acrylate medium rather than slowing it down, unlike quinacridone or phthalocyanines, which is also in agreement with similar studies found in the literature [4], [6], [19]. Since the acrylate paints exhibit characteristic peaks only below m/z 100 in the positive-ion mode of MeV-SIMS spectra [17], the occurrence of detectable species in the higher mass region of aged acrylate paints significantly aids detection and identification of acrylate species in real aged paints. The same can be concluded for the interpretation of MeV-SIMS spectra of the aged alkyd paints where several characteristic alkyd degradation products can be characterized as markers in MeV-SIMS measurements.
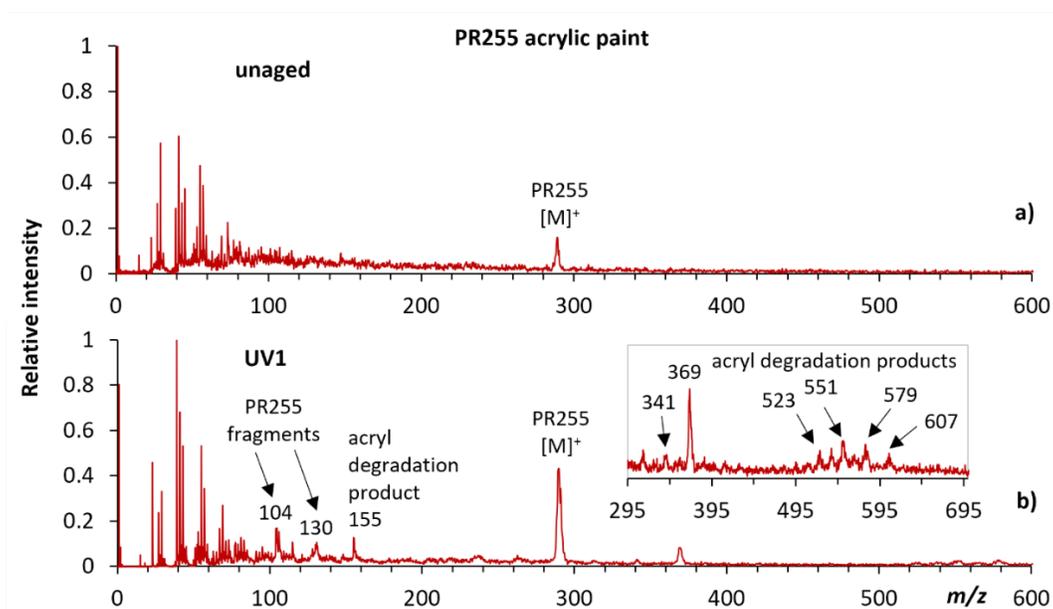
Fig. 6. MeV-SIMS spectra (5 MeV Si^{4+}, positive-ion mode) of the self-made acrylic paint with PR255: unaged (a), and two-month aged paint, UV1 (b); the m/z region between 295 and 700 where the characteristic degradation products are observed is also presented as in insert (b).

Table 2. List of characteristic peaks in the MeV-SIMS spectra (5 MeV Si^{4+} primary ion beam, positive-ion mode) of the four-month aged (UV2) alkyd and acrylic paints. Molecular ion peaks of SOPs are denoted in bold, binder-degradation product peaks in italic, and pigment and binder-characteristic fragment peaks in the regular font style.

Pigment	Alkyd paint*		Acrylic paint*	
	Pigment-characteristic peaks (*m/z*)	Alkyd-related peaks (*m/z*)	Pigment-characteristic peaks (*m/z*)	Acryl-related peaks (*m/z*)
PB15:1	63, 65, 102, 103, 129, 152, 154, 191, 193, **575**, **609**, **611**	105, *155*	191, 193, **576**, **610**	*288*
PB15:3, PB15:6	63, 65, 102, 103, 129, 152, 154, 165, 167, 191, 193, **575**	105, *155, 173, 327, 482*	191, 193, **576**	*155* (low)
PB16	102, 103, 129, **514**	*155, 173, 327, 482*	129, **514**	*155* (low)
PG7	63, 65, 266, 294, 330, **986**, 1021, **1056**, 1093, **1127**	*149, 155, 173, 327, 482*	63, 65, 328, **986**, **1055**, **1127**	none
PV19	256, 284, 296, **313**	105, *155, 173, 327, 482*	285 (low), 296 (low), **313**	*150, 155*
PR122	269, 284, 296, 313, **341**	149 (low), *155, 173, 327, 482*	N/A	N/A
PR254	111, 113, 138, 140, 164, **358**	*149, 155, 173, 327, 482*	138 (low), **358**	*155, 239, 267, 313, 341, 369, 523, 537, 551, 565, 579, 607*
PR255	104, 130, 235, 262, **289**	149 (low), *155, 173, 327, 482*	104, 130, 235, 262, **289**	*155, 313, 341, 369, 523, 537, 551, 579, 607*

*For the interpretation of the MeV-SIMS spectra of unaged SOPs and binders see Krmpotić et al. [17].

3.2 "MNB" painting analysis

Two samples of the blue and black paints from the acrylic painting "MNB" by Julije Knifer were analyzed with MeV-SIMS to assess if SOPs and binder could be identified in the artwork that is considered to have undergone exposure to environmental conditions. The obtained mass spectra are presented in Figure 7. Spectra of the blue and black samples overlap in the entire mass region with slight variations in peak relative intensities and ratios. Contamination of the sample surface with PDMS was evident through detection of species at *m/z* 73, 147, 207, 221, and 281 [16], [17], which was probably introduced during the sample preparation procedure. Spectral similarities between the blue and black samples indicate that only the binder component of the paint is detected, and that most probably inorganic pigments were used by the artist. Detected peaks at *m/z* 239, 313, 340, 369, 523, 537, 551, 565, 579, and 607 in the mass spectra could be assigned to the degradation products of the acrylate medium as they correspond to the species found in the studied aged DPP acrylate paints. Additional peaks detected in the mass region between *m/z* 200 and 700 (at *m/z* 257, 284) could derive from the species formed due to prolonged ageing (it is an almost 50-year-old painting) or from other additives in the paint. The presence of nBA and/or MMA as one of the polymeric components is highly possible, more so as most acrylic emulsion paints are based on p(nBA-MMA) copolymers. But the possibility of a similar acrylate copolymer should also be considered as the detected unidentified species could belong to degradation products of a different type of acrylate copolymer (e.g., acrylic copolymers containing 2-EHA or EA components).
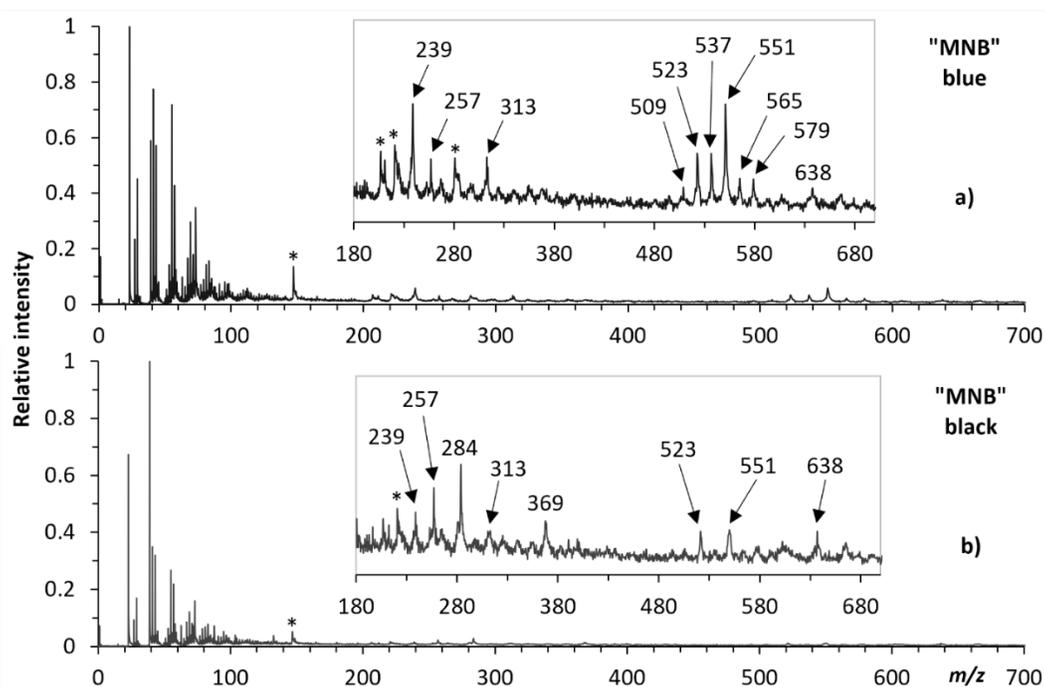
Fig. 7. MeV-SIMS spectra (5 MeV Si^{4+}, positive-ion mode) of the blue (a), and black (b) paints sampled from the "MNB" painting. Peaks denoted with * derive from PDMS contaminant, originating from the sample preparation process. The *m/z* region between 180 and 700, where lower intensity peaks are detected, is also presented for each spectrum as an insert.

Inorganic pigments were confirmed in both samples with micro-PIXE elemental analysis. Ultramarine pigment ($Al_6Na_8O_{24}S_3Si_6$) was identified and additionally confirmed with Raman spectroscopy [28] in the blue paint, with K, Ca, Ti, and Fe also being present. The reported photocatalytic degradation of binding media in ultramarine blue paint layers could explain the higher relative intensities of the peaks corresponding to acryl degradation products in the mass spectrum of the blue compared to the black paint [29]. The black paint sample was found to contain higher amounts of Fe and Ti, along with Al, Si, S, K, and Ca, which could correspond to the ferric oxide black pigment PBk11. This is a synthetic iron oxide pigment which is very resistant to weathering and likely to have been used by the artist. Hydrated aluminum silicate and gypsum may be present as extenders. Titanium found in both samples could indicate that titanium white was used in the paint mixtures.

3.3 "Plavi cvijet" outdoor sculpture analysis

The paint cross-section from the outdoor sculpture "Plavi cvijet", that was measured with MeV-SIMS, consisted of three distinct layers: the blue surface layer (topcoat), a white-bluish intermediate layer, and a brown-red ground layer (primer). Two SOPs were identified in the sample: CuPh PB15:3 through detection of the protonated molecular ion [M+H]$^+$ at *m/z* 576 and its strongest characteristic fragment $C_8H_4CuN_2^+$ at *m/z* 191, and dioxazine violet PV23 through the [M+H]$^+$ ion peak at *m/z* 589. Copper phthalocyanine blue PB15:3 (*β*-form) has a stimulated commercial value due to the highest thermodynamic stability of the unsubstituted CuPh polymorphs [30]. It is the most commonly used CuPh pigment [31] and for this reason was assigned to the analyzed paint although its mass spectrum is identical to that of PB15:6. The PB15:6 (*ε*-form) is present in contemporary artworks to a much lesser extent [31]. Pigment violet 23 is commercially one of the most representative dioxazine pigments which is often added to phthalocyanine blue to produce a reddish shade [30]. These SOPs were detected in the blue surface layer as well as in the white intermediate layer, but with lower relative abundance than in the blue region (Figure 8a and 8b). This was expected since the white layer contained dispersed blue pigment grains. Characteristic peaks at *m/z* 208 and 224 could be assigned to Pb$^+$ and PbO$^+$ species that were also detected

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in the surface and intermediate regions and could indicate the presence of inorganic lead pigment in the paint mixture, such as lead white [32], or may derive from oil containing lead soaps that might have been added as a corrosion inhibitor. The alkyd binding medium was identified through the detection of strong characteristic peaks at *m/z* 105 and 149 (Figure 8) in all three layers of the paint. The expected alkyd degradation products were observed at *m/z* 155 and 327 and were detected only in the surface layer of the paint but with low relative intensities. This demonstrates that the paint's chemical structure has been well preserved despite the sculpture being exhibited outdoors, and certainly exposed to environmental conditions. The reason for the increased chemical stability could be attributed to the high photostabilizing effect of phthalocyanine pigment present in the paint. However, this artwork is the most recent of all analyzed samples, which could also be the reason for minor degradation of the paint. Species in the higher mass region at *m/z* 495, 521, and 549 were detected only in the intermediate and the ground layer which could be assigned to diglycerides of oleic-suberic, linoleic-sebacic, and palmitic-palmitoleic acids, respectively [33].
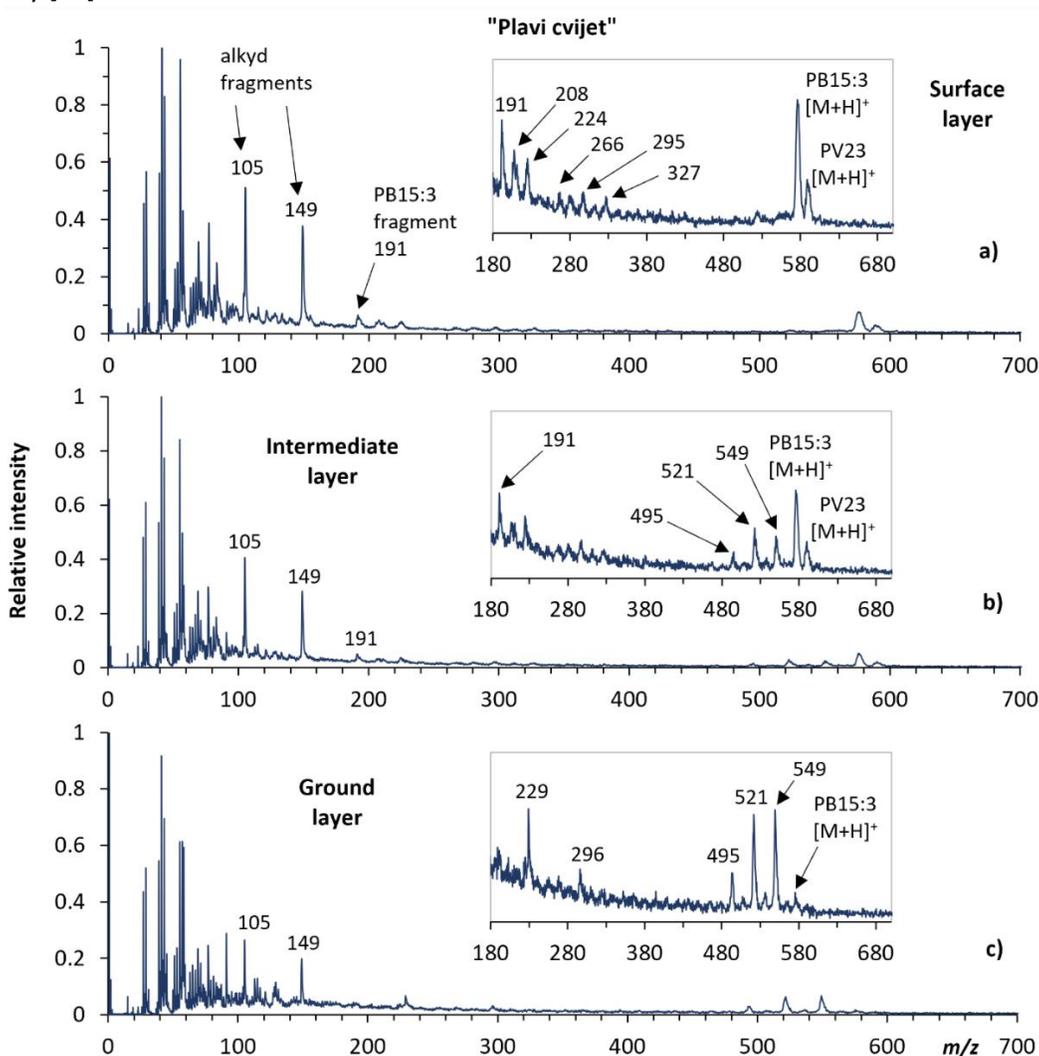
Fig. 8. MeV-SIMS spectra (8 MeV Si^{4+}, positive-ion mode) of the paint cross-section sampled from the "Plavi cvijet" outdoor sculpture: surface blue paint layer (a), intermediate white-bluish layer (b), and ground red-brown layer (c). The *m/z* region between 180 and 700, where lower intensity peaks are detected, is also presented for each spectrum as an insert.

3.4 "La dolcezza dell'abisso" mural painting analysis

In the blue paint sample taken from the "La dolcezza dell'abisso" mural painting, the PB15:1 pigment was identified with MeV-SIMS through detection of the protonated molecular ion peaks [M+H]$^+$ at *m/z* 576 and 609, and the characteristic fragment at *m/z* 191, 193 (Figure 9). Other characteristic peaks, which could not be associated with an acrylic medium, were detected at *m/z* 113, 115, 169, and 225 and could correspond either to the binder of a different composition than the ones studied in this work or to other components of the paint (additives). Additional measurements by FTIR and Py-GC/MS identified polyvinyl acetate (PVA) VeoVa polyvinyl ester as binders (spectra not presented in this work). Other components, such as kaolinite, calcite, and whewellite, were also found to be present in the sample.
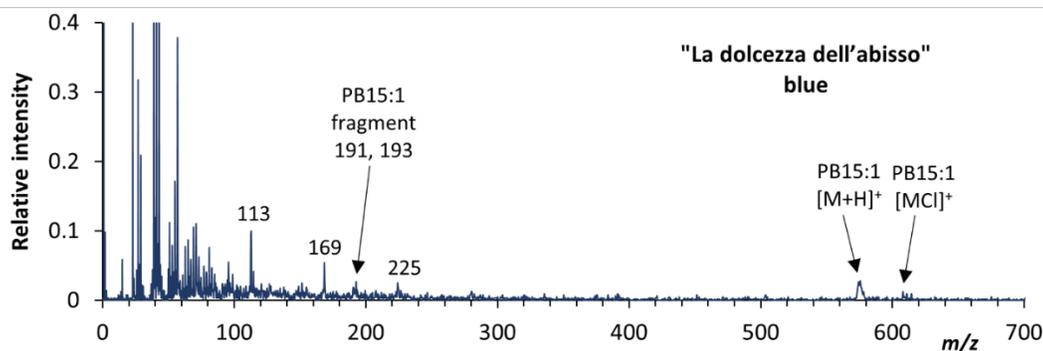
Fig. 9. MeV-SIMS spectrum (5 MeV Si^{4+}, positive-ion mode) of the blue paint sampled from the "La dolcezza dell'abisso" mural painting.

4. Conclusion

The MeV-SIMS results for the study of photodegradation of modern artists' paints are presented. Two-component paints containing an alkyd or acrylic binder mixed with phthalocyanine (PB15:1, PB15:3, PB15:6, PB16, and PG7), quinacridone (PV19 and PR122), and diketopyrrolo-pyrrole (PR254 and PR255) pigments were prepared and exposed to artificial UV ageing conditions. The SOPs molecular ions and characteristic fragment peaks were detected in the mass spectra of all aged two-component paints. Since no additional pigment-related fragments were detected in the surface layer of the aged paints compared to the unaged ones, it can be assumed that no significant changes in pigment structures occurred during ageing. This confirms that the pigments are stable under the accelerated solar ageing conditions, leading to a straightforward identification in aged paints. Chemical changes that were observed with MeV-SIMS through the detection of new species in the mass spectra can be assigned to the formation of photodegradation products from the alkyd and acrylic components of the paints, resulting in the enrichment of the pigment relative to the binder on the paint surface. Acrylic binder exhibited slightly higher stability to photodegradation compared to the alkyd medium, while the kinetics of the degradation processes were found to be dependent on the pigment present in the paint. Phthalocyanine pigments exhibited a high photostabilizing effect on both polymeric resins, while DPP pigments seem to promote degradation of the acrylate medium compared to phthalocyanine and quinacridone pigments.

The obtained results enabled the identification of SOPs and binders in original art objects that were expected to have undergone natural ageing. In the "MNB" (1970) painting samples, the acrylic binding medium was identified through detection of acryl-characteristic degradation products. The mass spectra indicated that most probably inorganic pigments were used by the artist, which was confirmed with micro-PIXE elemental analysis. Ultramarine blue and iron black pigments were identified as most probable. In the cross-section paint sample from the "Plavi cvijet" (2000) outdoor sculpture, the PB15:3 and PV23 SOPs were identified in the surface blue layer and white-bluish intermediate layer. Alkyd binder was identified in all three layers of the paint. Detection of strong alkyd-characteristic fragments in the surface layer showed that the paint had not gone through a significant photodegradation process despite being

exhibited outdoors, most probably due to the presence of the photostabilizing phthalocyanine pigment. The blue CuPh pigment PB15:1 was identified in the "La dolcezza dell'abisso" (1991) mural paint sample. Due to the lack of MeV-SIMS reference spectra for synthetic organic binders other than the studied alkyd and acrylic, the binding medium could not be identified based on the data obtained in this work.

Results of this research will significantly facilitate the interpretation of MeV-SIMS spectra for real case studies concerning the investigation of synthetic paint materials from modern and contemporary artworks that were exposed to environmental conditions or are of older date.

References

[1] T. Learner, A review of synthetic binding media in twentieth-century paints. *The Conservator*, **24** (2000) 96–103. https://doi.org/10.1080/01410096.2000.9995156

[2] S. Q. Lomax and T. Learner, A review of the classes, structures, and methods of analysis of synthetic organic pigments. *J. Am. Inst. Conserv*. **45** (2006) 107–125. https://doi.org/10.1179/019713606806112540

[3] N. Macro, M. Ioele, and M. Lazzari, A simple multi-analytical approach for the detection of oxidative and biological degradation of polymers in contemporary artworks. *Microchem. J*. **157** (2020) 104919. https://doi.org/10.1016/j.microc.2020.104919

[4] A. Ciccola, I. Serafini, M. Guiso, F. Ripanti, F. Domenici, F. Sciubba, P. Postorino, and A. Bianco, Spectroscopy for contemporary art: Discovering the effect of synthetic organic pigments on UVB degradation of acrylic binder," *Polym. Degrad. Stab*. **159** (2019) 224–228. https://doi.org/10.1016/j.polymdegradstab.2018.11.027

[5] M. Cocca, L. D'Arienzo, L. D'Orazio, G. Gentile, and E. Martuscelli, "Polyacrylates for conservation: chemico-physical properties and durability of different commercial products. *Polym. Test*. **23** (2004) 333–342. https://doi.org/10.1016/S0142-9418(03)00105-3

[6] M. Anghelone, V. Stoytschew, D. Jembrih-Simbürger, and M. Schreiner, Spectroscopic methods for the identification and photostability study of red synthetic organic pigments in alkyd and acrylic paints. *Microchem. J*. **139** (2018) 155–163. https://doi.org/10.1016/j.microc.2018.02.029

[7] Y. Zhao, J. Wang, A. Pan, L. He, and S. Simon, Degradation of red lead pigment in the oil painting during UV aging. *Color Res. Appl*. **44** (2019) 790–797. https://doi.org/10.1002/col.22386

[8] V. Pintus and M. Schreiner, Characterization and identification of acrylic binding media: Influence of UV light on the ageing process. *Anal. Bioanal. Chem*. **399** (2011) 2961–2976. https://doi.org/10.1007/s00216-010-4357-5

[9] C. Duce, V. Della Porta, M. R. Tiné, A. Spepi, L. Ghezzi, M. P. Colombini, and E. Bramanti, FTIR study of ageing of fast drying oil colour (FDOC) alkyd paint replicas. *Spectrochim. Acta A*. **130** (2014) 214–221. https://doi.org/10.1016/j.saa.2014.03.123

[10] C. Duce, L. Bernazzani, E. Bramanti, A. Spepi, M. P. Colombini, and M. R. Tiné, Alkyd artists' paints: Do pigments affect the stability of the resin? A TG and DSC study on fast-drying oil colours. *Polym. Degrad. Stab*. **105** (2014) 48–58. https://doi.org/10.1016/j.polymdegradstab.2014.03.035

[11] M. Anghelone, Influence of synthetic organic pigments on the photostability of alkyd and acrylic paints Hansa yellow, phthalo blue and phthalo green pigments: characterization and degradation. Doctoral Thesis, Academy of Fine Arts Vienna, 2017.

[12] M. Anghelone, D. Jembrih-Simbürger, V. Pintus, and M. Schreiner, Photostability and influence of phthalocyanine pigments on the photodegradation of acrylic paints under accelerated solar radiation. *Polym. Degrad. Stab*. **146** (2017) 13–23. https://doi.org/10.1016/j.polymdegradstab.2017.09.013

[13] S. Wei, V. Pintus, and M. Schreiner, A comparison study of alkyd resin used in art works by Py-GC/MS and GC/MS: The influence of aging. *J. Anal. Appl. Pyrolysis* **104** (2013) 441–447. https://doi.org/10.1016/j.jaap.2013.05.028

[14] B. N. Sundberg, R. Pause, I. D. van der Werf, A. Astefanei, K. J. van den Berg, and M. R. van Bommel, Analytical approaches for the characterization of early synthetic organic pigments for artists' paints. *Microchem. J*. **170** (2021) 106708. https://doi.org/10.1016/j.microc.2021.106708

[15] M. C. Malloy, I. Bogdanović Radović, Z. Siketić, and M. Jakšić, Determination of deposition order of blue ballpoint pen lines by MeV Secondary Ion Mass Spectrometry. *Forensic Chem*. **7** (2018) 75–80. https://doi.org/10.1016/j.forc.2017.10.004

[16] I. Bogdanović Radović, Z. Siketić, D. Jembrih-Simbürger, N. Marković, M. Anghelone, V. Stoytschew, and M. Jakšić, Identification and imaging of modern paints using Secondary Ion Mass Spectrometry with MeV ions. *Nucl. Instrum. Methods Phys. Res. B* **406** (2017) 296–301. https://doi.org/10.1016/j.nimb.2017.01.007

[17] M. Krmpotić, D. Jembrih-Simbürger, Z. Siketić, N. Marković, M. Anghelone, T. Tadić, D. Plavčić, M. Malloy, and I. Bogdanović Radović. Identification of Synthetic Organic Pigments (SOPs) Used in Modern Artist's Paints with Secondary Ion Mass Spectrometry with MeV Ions. *Anal. Chem*. **92** (2020) 9287–9294. https://doi.org/10.1021/acs.analchem.0c01630

[18] B. N. Jones, J. Matsuo, Y Nakata, H. Yamada, J. Watts, S. Hinder, V. Palitsin, and R. Webb, Comparison of MeV monomer ion and keV cluster ToF-SIMS. *Surf. Interface Anal*. **43** (2011) 249–252. https://doi.org/10.1002/sia.3520

[19] M. Anghelone, D. Jembrih-Simbürger, and M. Schreiner, Influence of phthalocyanine pigments on the photo-degradation of alkyd artists' paints under different conditions of artificial solar radiation. *Polym. Degrad. Stab*. **134** (2016) 157–168. https://doi.org/10.1016/j.polymdegradstab.2016.10.007

[20] T. Tadić, I. Boganović Radović, Z. Siketić, D. D. Cosic, N. Skukan, M. Jakšić, and J. Matsuo, Development of a TOF SIMS setup at the Zagreb heavy ion microbeam facility. *Nucl. Instrum. Methods Phys. Res. B* **332** (2014) 234–237. https://doi.org/10.1016/j.nimb.2014.02.068

[21] M. Bogovac, I. Bogdanović, S. Fazinić, M. Jakšić, L. Kukec, and W. Wilhelm, Data acquisition and scan control system for nuclear microprobe and other multiparameter experiments. *Nucl. Instrum. Methods Phys. Res. B* **89** (1994) 219–222. https://doi.org/10.1016/0168-583X(94)95176-4

[22] D. Cosic, M. Bogovac, and M. Jakšić, Data acquisition and control system for an evolving nuclear microprobe. *Nucl. Instrum. Methods Phys. Res. B* **451** (2019) 122–126. https://doi.org/10.1016/j.nimb.2019.05.047

[23] M. Strohalm, M. Hassman, B. Košata, and M. Kodíček, mMass data miner: an open source alternative for mass spectrometric data analysis. *Rapid Commun. Mass Spectrom*. **22** (2008) 905–908. https://doi.org/10.1002/rcm.3444

[24] I. S. Gilmore and M. P. Seah, Ion detection efficiency in SIMS: dependencies on energy, mass and composition for microchannel plates used in mass spectrometry. *Int. J. Mass Spectrom*. **202** (2000) 217–229. https://doi.org/10.1016/S1387-3806(00)00245-1

[25] V. Pintus, S. Wei, and M. Schreiner, Accelerated UV ageing studies of acrylic, alkyd, and polyvinyl acetate paints: Influence of inorganic pigments. *Microchem. J*. **124** (2016) 949–961. https://doi.org/10.1016/j.microc.2015.07.009

[26] F. X. Perrin, M. Irigoyen, E. Aragon, and J. L. Vernet, Artificial aging of acrylurethane and alkyd paints: A micro-ATR spectroscopic study. *Polym. Degrad. Stab*. **70** (2000) 469–475. https://doi.org/10.1016/S0141-3910(00)00143-9

[27] A. Ciccola, M. Guiso, F. Domenici, F. Sciubba, and A. Bianco, Azo-pigments effect on UV degradation of contemporary art pictorial film: A FTIR-NMR combination study. *Polym. Degrad. Stab*. **140** (2017) 74–83. https://doi.org/10.1016/j.polymdegradstab.2017.04.004

[28] D. Plavčić, Identification and molecular imaging of modern paint materials using MeV SIMS for forensic purpose. Diploma Thesis, University of Zagreb, 2018.

[29] E. R. de la Rie, A. Michelin, M. Ngako, E. Del Federico, and C. Del Grosso, Photo-catalytic degradation of binding media of ultramarine blue containing paint layers: A new perspective on the phenomenon of "ultramarine disease" in paintings. *Polym. Degrad. Stab*. **144** (2017) 43–52. https://doi.org/10.1016/j.polymdegradstab.2017.08.002

[30] W. Herbst and K. Hunger, Industrial Organic Pigments: Production, Properties, Applications. Third Edition, Wiley-VCH, Weinheim, 2004.

[31] C. Defeyt and D. Strivay, PB15 as 20th and 21st Artists' Pigments: Conservation Concerns. *E-Preservation Sci*., **11** (2014) 6–14.

[32] K. Keune and J. J. Boon, Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden. *Anal. Chem*. **76** (2004) 1374–1385. https://doi.org/10.1021/ac035201a

[33] T. Vande Moortel, Contributions to the study of oil based binding media with ToF-SIMS. Masters dissertation, École polytechnique de Louvain (EPL), 2016.